



FTIR study of photocatalytic degradation of 2-propanol in gas phase with different TiO₂ catalysts

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ABSTRACT

The photocatalytic efficiency of different TiO₂ catalysts in the degradation of 2-propanol in gas phase has been studied. The obtained efficiencies have been compared considering the distribution of rutile–anatase phases, surface area, particle size, distribution of surface hydroxyl groups and Brønsted or Lewis acid centres. The catalysts used were Degussa-P25 (TiO₂-P25), Hombikat, Millennium, Kemira and s/g-TiO₂, a catalyst prepared by a sol–gel method.

The best photocatalytic behaviours have been obtained with those catalysts with higher surface area and the presence of only anatase phase (Hombikat and Millennium). A progressive deactivation of TiO₂-P25 and s/g-TiO₂ has been observed during the photocatalytic process.

FTIR studies indicated that degradation mechanisms depended on the catalyst employed. Deactivation processes observed in TiO₂-P25 have been correlated with the formation of carboxylates.

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1. Introduction

The treatment of wastewater containing toxic organic compounds by photocatalytic process has been mainly studied with TiO₂. Of the four polymorphic structures of naturally occurring TiO₂, anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and TiO₂ (B) (monoclinic), only the first two phases present photoactivity. Differences in lattice of these two TiO₂ crystalline phases produce different densities and structures of the electronic bands, giving rise to different band gaps (3.2 eV anatase and rutile 3.02 eV). Thus, the absorption threshold of anatase and rutile in well crystallized samples appears at 384 and 410 nm, respectively [1]. It has also been indicated that the mobility of photogenerated electrons is different in both phases because anatase is 9% less dense than rutile [2,3]. On the other hand, in view of the different structures, the surface chemistry is expected to be significantly different for anatase and rutile.

Different studies conducted in the aqueous phase with this semiconductor catalysts have shown that those with an anatase: rutile ratio equal to 3–4:1 were better photocatalysts. In catalysts with such a phase ratio as the commercial catalyst Degussa P-25 the existence of an interaction between the two phases enhances the electron–hole separation and increases the total photoeffi-

ciency [4–6]. This indicates that electron photogenerated in active centres of anatase migrates to the rutile phase due to the appropriate relative levels between Fermi anatase and rutile which can help charge separation [3]. However, not all catalysts with the same rutile–anatase proportion present the same photocatalytic activity, which has also been related to the particle size, surface area of the catalyst or even the pH of the solution [4]. Thus, in aqueous solution these other parameters have also been considered to be vital. Consequently, it has been suggested that the particle size can influence the flow rate of photons transmitted [7]. Moreover, it has been suggested that the photoactivity of titanium dioxide particles increases linearly with increasing the crystallite size of anatase phase as long as no significant rutile phase was formed. Additionally, it was proved that the photoactivity of this semiconductor is supposed to be enhanced by increasing the surface area while keeping a similar crystallite size [8].

The higher photoactivity of Degussa P-25 in aqueous phase with respect to other catalysts with only anatase has been shown in numerous studies. Thus, its activity has been compared to those of commercial catalysts containing only the anatase phase, a much larger surface area and a slightly smaller particle size, such as Millennium or Hombikat. In most of these studies the efficiency of Degussa P-25 has been higher [9–14].

As noted above, studies in aqueous phase have shown the higher efficiency of Degussa P-25 over other catalysts with only anatase phase as Hombikat or Millennium. Moreover, most of these studies have been mainly focused on the catalyst bulk

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properties, however a greater emphasis must be given to the surface properties of the catalysts.

On the other hand, in gas phase comparative studies between Degussa P-25 and Hombikat or Millennium have not yet been carried out. In this regard, comparative studies between Degussa P-25 and nanosized TiO₂ catalysts with different specific surface area have been conducted in the gas phase with hexane, methanol and benzene [15] or between Degussa P-25 and anatase brookite-mixed powders in the degradation of toluene [16] in which different behaviours were observed depending on the substrate analyzed. Therefore, photocatalytic studies in gas phase to remove volatile organic compounds have been gradually developing in the last few years [17–21]. These studies have improved important aspects such as reactor configuration, catalysts support and physical–chemical parameters that affect the efficiency of these processes in the gas phase.

In this manuscript the efficiency of Degussa P-25 at the photocatalytic degradation of 2-propanol in gas phase is compared to that of other catalysts with only anatase and different surface areas. 2-Propanol has been used by other authors as model compound to compare the efficiency of Degussa P-25 to that of doped TiO₂ in the gas phase. Depending on the dopant used better efficiencies could be obtained [22–24]. It has also been used to compare Degussa P-25 to catalysts prepared by new methods of synthesis or with peroxo titanium complexes [25–28].

A catalyst with only rutile has also been studied and compared. These studies have been conducted to determine if the efficiency of Degussa P-25 in gas phase is also higher than that of the previous catalysts as it is in the aqueous phase.

2. Experimental

2.1. Catalyst preparation

Photocatalytic activity studies in gas phase have been performed with different commercial TiO₂ catalysts: Degussa P-25 (TiO₂-P25), Hombikat UV100 (Hombikat), Millennium PC100 (Millennium) and Kemira 650 (Kemira). All of them were used as received. In addition to this, a catalyst named as (s/g-TiO₂) was prepared by a sol–gel method using titanium tetraisopropoxide (TIP) as a precursor in isopropanol (3.9 ml in 200 ml iPrOH TIP). Hydrolysis of the isopropanol–TIP solution was achieved by adding certain volume of bidistilled water (200 ml). Precipitates were then filtered and dried at 120 °C overnight. The catalyst was calcined in air at 500 °C for 2 h.

BET surface area measurements were carried out by N₂ adsorption at 77 K using a Micromeritics 2000 instrument.

X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu K α radiation. Anatase/rutile fractions were calculated by taking into account the relative diffraction peak intensities. From the line broadening of corresponding X-ray diffraction peaks, the mean crystallite size according to the Scherrer equation (peaks were fitted by using a Voigt function) was calculated:

$$D = \lambda \times 180\pi \times \cos\theta \times L$$

where L is the line width at medium height, λ the wavelength of the X-ray radiation 0.15406 nm and θ the diffracting angle.

2.2. Experimental conditions

All the experiments were carried out in a continuous reactor device at 35 °C. This system consists of a vessel containing a 2:1 (v/v) water–2-propanol solution. This vessel was continuously air-bubbled at a flow rate of 2 cm³/min. The relative humidity of the influent gas was constant throughout the study at 100%. The resulting air containing water and 2-propanol vapours was introduced in five 15-cm long, 4-mm diameter cylindrical glass reactors containing the catalyst (packed-bed reactor). Only the outer portion of the catalyst in contact with the inner wall of the reactor is exposed to the light and hence will be reactive. In order to compare their catalytic activities, the reactor was filled up to the same height (10-cm) with all catalysts. Thus, similar contact times were obtained [29]. A 2-propanol/water mixture was passed through the reactor for 24 h prior irradiation with the aim of saturating the surface of the catalysts.

2.3. Equipment

The exhaust gases were continuously analysed by means of a GC (Varian Star 3600) equipped with a gas injection valve and a FID detector to determine 2-propanol and its reaction products. Additionally, a TCD detector was used to determine CO₂. The GC injection valve was equipped with a 50- μ l loop and a supelco SPB-1 capillary column (30 m \times 0.32 mm \times 0.25 μ m) for monitoring and calibration of 2-propanol and its intermediates. A catalytic chamber was employed to monitor intermediates on the catalyst surface by means of FTIR spectroscopy.

FTIR studies in cell with CaF₂ windows, where samples were located, were carried out in a FTIR spectrophotometer model RS/1 from UNICAM. Water reference spectrum was always subtracted from every spectrum in the region between 1800 and 1000 cm^{−1}. For these studies FTIR samples were saturated with NH₃ (anhydrous) or 2-propanol using the gas system and then placed in the cells of CaF₂ maintaining reaction conditions.

3. Characterization studies

Table 1 summarizes XRD results, surface area analysis and particle size. Hombikat and Millennium present only the anatase phase in its crystal structure. Kemira presents only the rutile phase and TiO₂-P25 shows 80% of anatase phase and 20% rutile while s/g-TiO₂ is 99% of anatase.

TiO₂-P25, Kemira and s/g-TiO₂ present a similar particle size, around 22–25 nm. Instead, Millennium and Hombikat have a particle size slightly lower, 9 and 15 nm, respectively.

With regard to surface area, Hombikat provided the higher value (280 m²/g), Millennium presented a surface area about twice that the TiO₂-P25 and Kemira (90, 51 and 52 m²/g respectively). Finally, the surface area of s/g-TiO₂ was about half that of the TiO₂-P25 (28 m²/g).

Table 1
Phase composition, particle size and surface area of catalysts studied.

Catalyst	Phase composition %	Primary TiO ₂ particle size (nm)	Surface BET (m ² /g)
TiO ₂ -P25	80% (A)–20% (R)	22 (anatase)	51
Hombikat UV-100	100% (A)	9 (anatase)	280
Kemira 650	100% (R)	25 (rutile)	52
Millennium PC-100	100% (A)	15 (anatase)	90
s/g-TiO ₂	99% (A)	22 (anatase)	28

(A) anatase; (R) rutile.

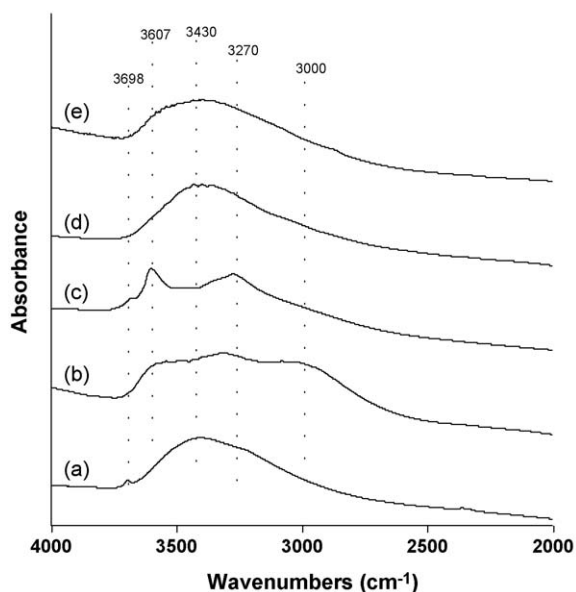


Fig. 1. FTIR spectra in the hydroxyl group region. (a) TiO₂-P25, (b) Hombikat, (c) Millennium, (d) s/g-TiO₂ and (e) Kemira.

Different studies have indicated a strong effect of particle size on photoactivity. It has been indicated that particle size can influence the efficiency of absorption, light scattering and charge-carrier dynamics. Thereby, the optimum particle size is a result of effective competing on light absorption, scattering efficiency, charge-carrier dynamics and surface area [30].

4. Characterization of surface hydroxyl groups

The nature and distribution of surface OH groups is in many cases the determining factor of TiO₂ behaviour [31–33]. These groups also provide adsorption centres for reagents and/or products and can be precursors of hydroxyl radicals responsible for many degradation processes. Thus, FTIR studies were performed to characterize the distribution of hydroxyl groups present on studied catalysts surface (Fig. 1).

Only TiO₂-P25 and Millennium showed the presence of isolated hydroxyl groups (band at 3698 cm⁻¹). These groups are usually present at vertices and defects on the catalyst surface and are considered to be the most basic and photoactive ones [34,35].

On the other hand, the spectra of these samples in the region between 3600 and 3000 cm⁻¹ are represented by different types of hydroxyl groups with different acid-base character and water molecules adsorbed through hydrogen bond [36]. Intermolecular H bonding was involved to act as stabilizing factor for a mixed dissociated/molecular state of water [37–39]. The spectra of Hombikat and Millennium in this region are very similar, showing a broad band of approximately the same intensity throughout the entire region. However, TiO₂-P25 and s/g-TiO₂ show a greater intensity of the band centred at 3430 cm⁻¹ which is attributed to weak surface active sites. At these points physisorbed water molecules are bound by weak hydrogen bonds to each other and/or to OH-group of TiO₂ surface [40]. Similar differences in the distribution of surface hydroxyl groups between TiO₂-P25 and Hombikat have been observed in other studies which have indicated that the number of moles of these groups per square meter is three times higher in TiO₂-P25 than in the Hombikat [41]. The largest concentration of surface hydroxyl groups in TiO₂-P25 has also been correlated with their greater capacity for oxygen adsorption with respect to Hombikat [41].

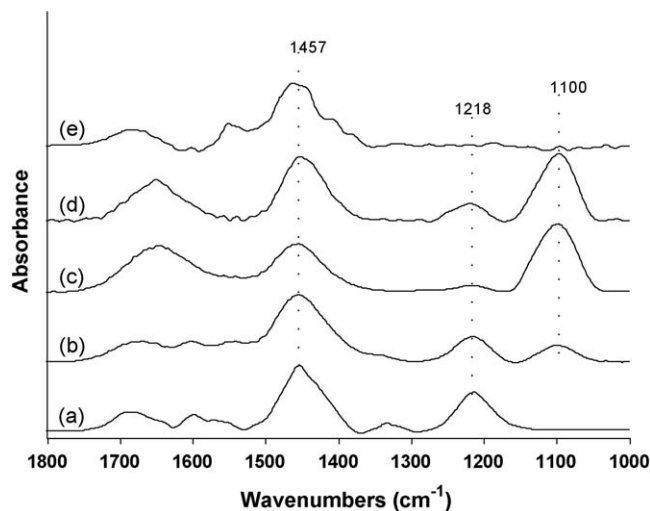


Fig. 2. FTIR spectra of NH₃ interaction. (a) TiO₂-P25, (b) Hombikat, (c) Millennium, (d) s/g-TiO₂ and (e) Kemira.

The spectrum from Kemira revealed the presence of hydroxyl groups albeit in a slightly different surface distribution. Thus, the relative intensity of the band at 3430 cm⁻¹ in Kemira was lower than that observed in TiO₂-P25 and s/g-TiO₂. However, in the region between 3200 and 3000 cm⁻¹ the three catalysts showed similar spectra.

5. Characterization of Lewis and Brönsted acid centres

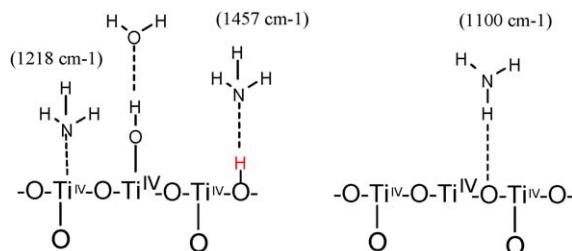
In order to complete the characterization of these catalysts, ammonia interaction with the catalysts surface has been studied (Fig. 2). Different studies have indicated that adsorption centres of this molecule can determine the presence of Lewis or Brönsted acid centres [42,43].

The interaction of anhydrous ammonia with all catalysts generated a band centred at 1457 cm⁻¹ which is attributed to the presence of NH₄⁺ adsorbed on Brönsted acid centres [44]. However, only TiO₂-P25, Hombikat, s/g-TiO₂ and Millennium showed a band centred at 1218 cm⁻¹ which is attributed to NH₃ adsorbed on Lewis acid centres [45,46]. The relative intensity of this band follows the sequence:

TiO₂ – P25 > Hombikat > s/g – TiO₂ ≫ Millennium

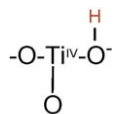
This seems to indicate a proportional greater presence of those centres in TiO₂-P25. Finally, only Hombikat, Millennium and s/g-TiO₂ presented a band centred at 1100 cm⁻¹. The relative intensity of this band was much lower in Hombikat with regard to the other two catalysts. This band has been attributed to the interaction of ammonia with oxygen atoms of the metal oxide surface [47].

Thus, different adsorptions forms of NH₃ on the catalysts studied, which are correlated with the Lewis or Brönsted acid centres, can be illustrated as:



The absence of the band at 1100 cm⁻¹ in TiO₂-P25 can be attributed to the high hydroxylation of the catalyst surface. This

band is not observed in the Kemira. The high degree of hydroxylation of TiO₂-P25 favours the presence of the centres



These centres can be stabilized by hydroxyl groups or water molecules. Thus, the concentration of centres to which NH₃ molecules can be attached directly with oxygen atoms of the metal oxide surface results minimized. In fact, as mentioned above the relative intensity of the band at 1457 cm⁻¹ was higher in TiO₂-P25.

Moreover, it should be emphasized that there is no apparent relationship between the distribution of these Lewis or Brönsted acid centres and the particle size or surface area of the catalysts. It should be noted that the band at 1100 cm⁻¹ appears in those catalysts containing only anatase.

6. Degradation studies of 2-propanol in gas phase

These studies have been performed in the reaction system indicated in Section 2. The results of these studies are shown in Fig. 3.

During the first 2 h of 2-propanol degradation with TiO₂-P25 (Fig. 3) the mineralization of the molecule was high (72%). However, at longer reaction times, mineralization was decreased and a gradual formation of acetone was noticed. In other words, it appears that this catalyst was progressively deactivated with time. Similar but faster deactivation processes have also been observed in studies in gaseous phase with methanol or ethanol with this catalyst [48,49]. Moreover, it should be noted the formation of trace amounts of propylene has been observed.

The behaviour of Hombikat was the opposite to that of TiO₂-P25, which showed (Fig. 3) a degradation increase with reaction

time, being mineralization complete after the first 15 h of reaction. Thus, a progressive activation of degradation centres seems to occur. Moreover, during the first 15 h only traces of intermediates, such as acetaldehyde, acetone and propylene were observed, i.e., notably lower concentrations than those obtained with TiO₂-P25.

The photocatalytic behaviour of Millennium was very similar to that observed with Hombikat, i.e., an increase of mineralization with the reaction time (Fig. 3). However, Millennium achieved a lower mineralization level than Hombikat, so that after 20 h of reaction the complete mineralization of 2-propanol in the reactors had not been achieved.

The catalyst s/g-TiO₂ showed a relative low grade of mineralization during the first 5 h of reaction and a total deactivation thereafter (Fig. 3). Finally, the catalyst Kemira did not achieve any degradation or mineralization. No propylene formation was noticed with Millennium, s/g-TiO₂ or Kemira.

At this stage, results demonstrate that the nature of catalyst produces different response of 2-propanol interaction, probably due to different nature of hydroxyl groups and active Lewis and Brönsted acid centres which generate different adsorption sites.

7. FTIR studies

7.1. Interaction of 2-propanol

The degradation studies in the gas phase with 2-propanol have shown remarkably different behaviours of the catalysts studied. These catalysts have different features in terms of rutile–anatase proportion, surface area and distribution of hydroxyl groups and Brönsted and Lewis acid centres. Therefore, to correlate the different photocatalytic activities observed with physical–chemical properties, 2-propanol interaction with catalysts surface and its behaviour during illumination have been studied with FTIR

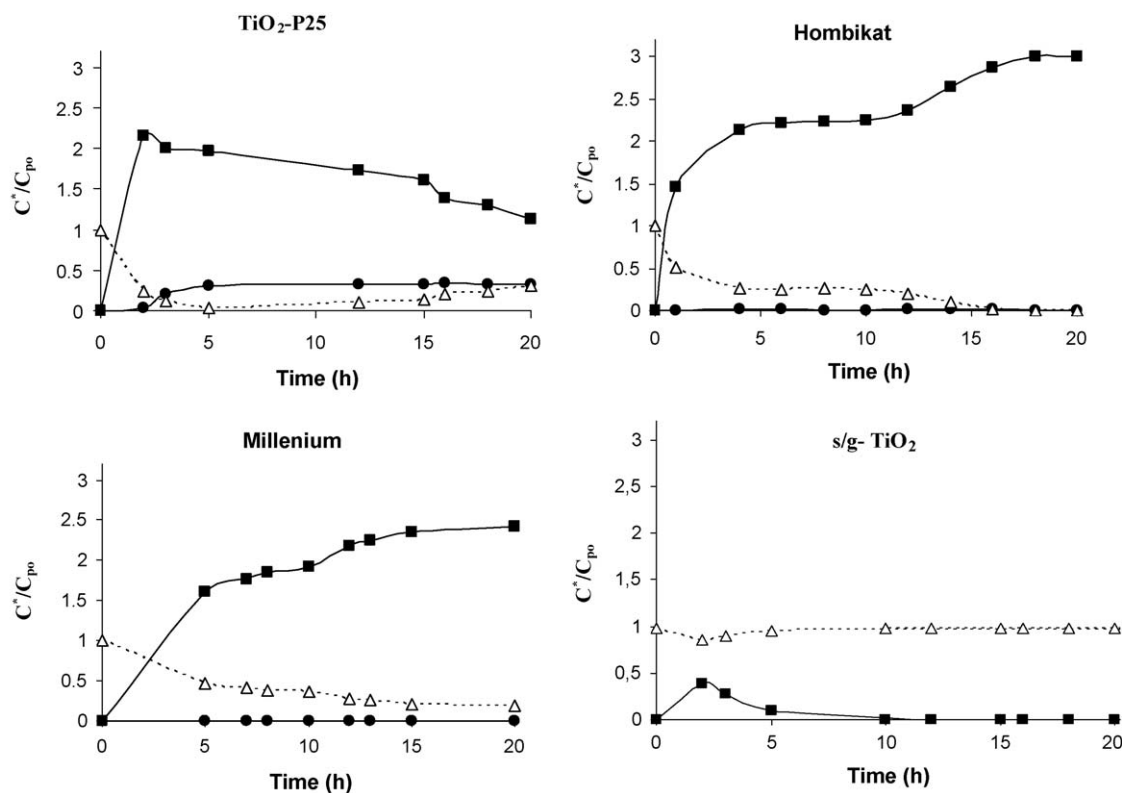


Fig. 3. Concentrations of 2-propanol (Δ), acetone (\bullet) and CO₂ (\blacksquare) during 2-propanol photocatalytic degradation with TiO₂-P25, Hombikat, Millennium and s/g-TiO₂. [C^*] = concentration of each compound, [C_{po}] = initial 2-propanol concentration.

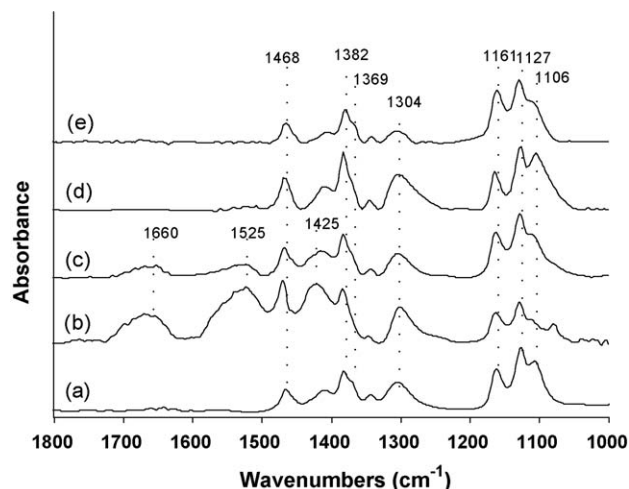


Fig. 4. FTIR reference spectrum of 2-propanol (a) and spectra of this alcohol interaction with TiO₂-P25 (b), Hombikat (c), Millennium (d) and s/g-TiO₂ (e).

spectroscopy. These studies have been carried out in CaF₂ cell windows following the procedure outlined in Section 2.

No adsorption of 2-propanol molecules to the surface of Kemira was observed. In Figs. 4 and 5 the spectra of 2-propanol interaction with the catalysts in the regions between 1800–1000 and 4000–2000 cm⁻¹ are compared. First, it must be stressed that the interaction of this molecule with TiO₂-P25 and Hombikat (Fig. 4b and c) leads to new bands at 1660, 1525 and 1425 cm⁻¹ which are not observed in the reference spectrum of 2-propanol (Fig. 4a). These bands are attributed to the dehydration of some of 2-propanol molecules adsorbed to produce propylene.

Different studies have indicated that the formation of propylene from 2-propanol is directly related to the presence of Brønsted or Lewis acid centres on the catalyst surface [44]. The characterization of these centres through the interaction of NH₃ conducted in the present study has shown that all the catalysts presented Brønsted acid centres. However, the presence of Lewis acid centres was clearly observed in TiO₂-P25, Hombikat and s/g-TiO₂.

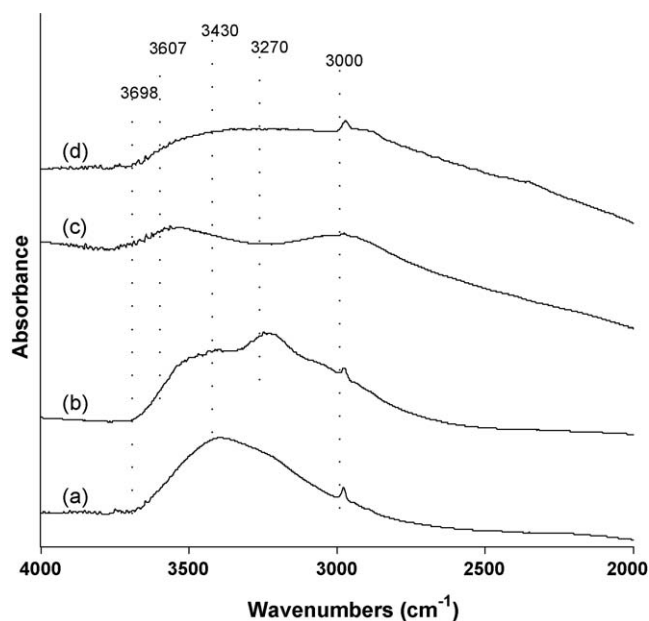


Fig. 5. FTIR spectra in the hydroxyl group region after 2-propanol interaction with: (a) TiO₂-P25, (b) Hombikat, (c) Millennium and (d) s/g-TiO₂.

Degradation and FTIR studies have shown the formation propylene in the first two catalysts. Therefore, from these results we can state that the formation of propylene under these conditions is primarily related to the presence of Lewis acid centres.

In TiO₂-P25, Hombikat and s/g-TiO₂, a decline in the relative intensity of the bands from 2-propanol interaction and the one at 1106 cm⁻¹ attributed to the νC–O vibration in which the presence of Lewis acid centres, was observed. This decrease is more intense in TiO₂-P25, in which even a new band at lower wavenumbers was detected. These changes in the interaction may be due to the different nature of adsorption centres which can influence the process of degradation.

Moreover, the spectra in the region between 4000 and 2000 cm⁻¹ after the interaction of 2-propanol (Fig. 5) shows that:

- in TiO₂-P25, the band at 3698 cm⁻¹ attributed to the hydroxyl groups isolated disappeared.
- in Hombikat, the relative intensity of the band centred at 3000 cm⁻¹ which is attributed to hydroxyl groups with stronger acid character is reduced.
- in Millennium and s/g-TiO₂, the relative intensity of the bands located in the region between 3430 and 3270 cm⁻¹ was diminished.

7.2. FTIR studies under illumination

Catalysts in which the adsorption of 2-propanol molecules was observed, were irradiated and analyzed by infrared spectroscopy. Figs. 6–11 show the spectra obtained under illumination in the region between 1800–1000 and 4000–2000 cm⁻¹. The spectra between 4000–2000 cm⁻¹ are shown after subtraction of the spectrum obtained during the previous lighting to observe more clearly the behaviour of the bands in this region under illumination.

7.3. Behaviour of 2-propanol adsorbed on TiO₂-P25 under illumination

After 2 min of illumination of TiO₂-P25, all 2-propanol adsorbed was oxidized to acetone (bands at 1709, 1375 and 1233 cm⁻¹) (Fig. 6b) and in the region of hydroxyl groups (Fig. 7a) a slight increase of the band attributed to the isolated hydroxyl groups (3698 cm⁻¹) and a decrease in intensity of the band centred at 3430 cm⁻¹ was observed. After 5 min of illumination, the intensity of the band attributed to acetone was decreased and new bands in

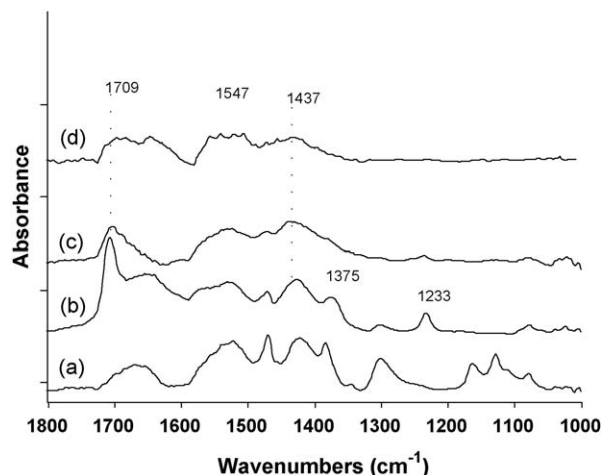


Fig. 6. FTIR spectra of 2-propanol adsorbed on TiO₂-P25 (a) and after 2 (b), 5 (c) and 15 (d) minutes of illumination.

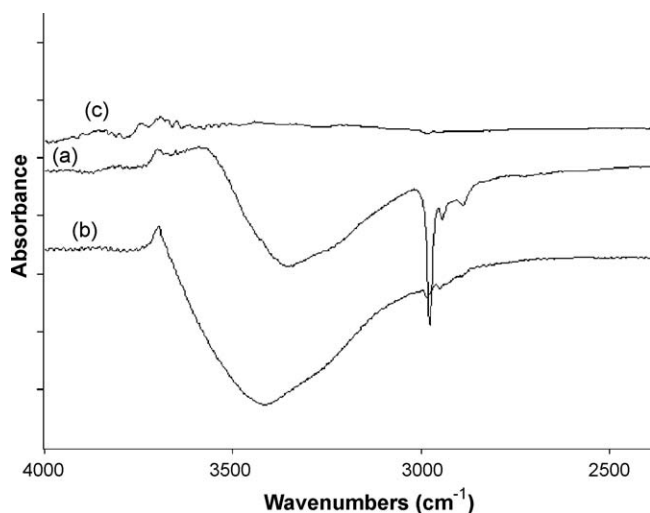
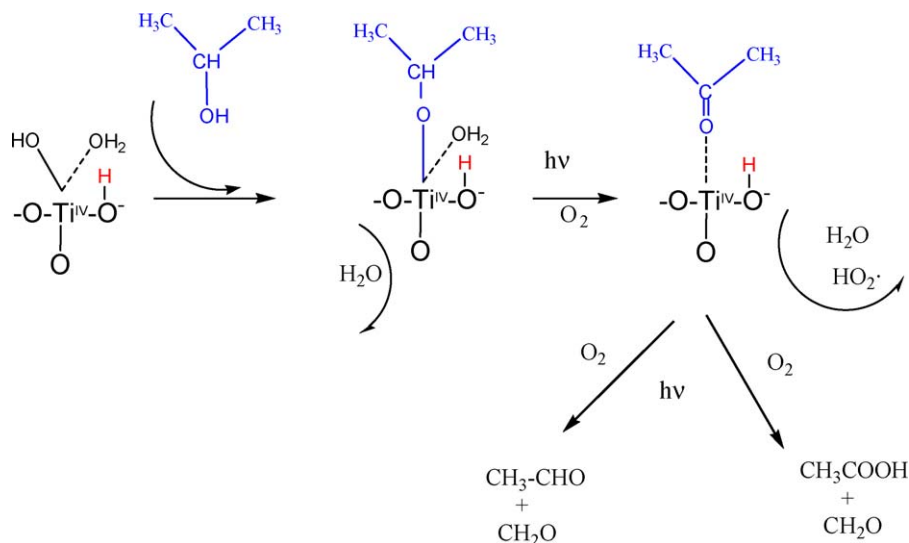


Fig. 7. Modification of relative intensity of FTIR spectra in the hydroxyl group region of TiO₂-P25 under illumination: (a) after the first 2 min, (b) between 2 and 5 min, and (c) between 5 and 15 min. These spectra have been obtained by subtracting that of the previous illumination period (shown in Fig. 6) from each spectrum.

the region between 1500 and 1400 cm⁻¹ that are attributed to acetates (Fig. 6c) appeared [49]. It should be noted that the intensity of bands attributed to acetates was less intense than expected from studies with other alcohol [48,49]. In the hydroxyl group region, isolated hydroxyl groups' intensity was increasing again and the band at 3450 cm⁻¹ was also diminished (Fig. 7b). No important changes were observed in the spectra when the sample was irradiated for longer time.

Different TiO₂ surface characterization studies indicate that Lewis acidic and basic centres can be present, depending on the exposed face (0 0 1), (1 0 0), etc. [37,50]. Consequently, Ti⁴⁺ atoms with 4, 5 or 6 coordination positions and O²⁻-lattice atoms with 2 or 3 can be found, depending on the surface exposed. Different faces can be exposed to possible distribution of hydroxyl groups and coordinated water in TiO₂ Degussa P-25. In this surface distribution, the following centre can be found, among others where Ti⁴⁺ is coordinated with a hydroxyl group (isolated from the others and responsible for the band at 3698 cm⁻¹, and with highly basic character (OH) [51,52], a water molecule, a hydroxyl group with acidic character and different O₂-lattice atoms to complete the coordination number (Scheme 1).



Scheme 1.

From this surface distribution, FTIR results have indicated that 2-propanol molecules interact primarily with the isolated hydroxyl groups of TiO₂-P25 (Fig. 5) (Scheme 1). When the catalyst was illuminated, 2-propanol adsorbed was oxidized to acetone, which was also observed in continuous studies and in those in the cell of CaF₂ by FTIR. Throughout this process generated HO₂[•] radical can evolve to H₂O₂.

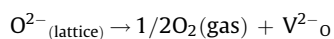
Acetone adsorbed under illumination can be degraded to acetaldehyde and formaldehyde or formaldehyde and acetic depending on the mechanism [53]. Acetaldehyde and formaldehyde do not seem to be adsorbed. However, acetic acid molecules are adsorbed onto the catalyst surface but at different points from those of 2-propanol because isolated hydroxyl groups were regenerated after its formation (Fig. 7). The progressive increase of acetate concentration on the catalyst surface may be responsible for its progressive deactivation as observed during degradation in continuous mode and the reduction of the hydroxyl group band at 3430–3450 cm⁻¹. In this sense, the high hydroxylation of the surface of this catalyst would facilitate oxygen molecules adsorption which in turn enhances the formation of O₂^{•-} radicals and consequently that of carboxylates [54,55].

Moreover, as indicated above, the intensity of the bands attributed to acetates observed on the catalyst surface after irradiation was lower than expected. This is attributed to the presence of another mechanism of degradation by means of H₂O₂ in which carboxylates are not generated.

7.4. Behaviour of 2-propanol adsorbed on Hombikat under illumination

Figs. 8 and 9 show the spectra, in the region between 1800–1000 and 4000–2000 cm⁻¹, respectively, of the behaviour 2-propanol adsorbed on Hombikat by illumination.

As can be seen, the oxidation of 2-propanol is much slower than that observed with TiO₂-P25 as 20 min were needed to achieve the total degradation of the alcohol (Fig. 8). The reactivity of many metal oxides has been related to their anionic sub stoichiometry M^{x+}O^{2-(x/2)±} (deficit in lattice O²⁻ anions) accounted for by the existence of anionic vacancies V²⁻_O.



V²⁻_O corresponds to a neutral entity with respect to the lattice (also called neutral helium centre). In this regard, various studies have indicated that the presence of surface oxygen deficient

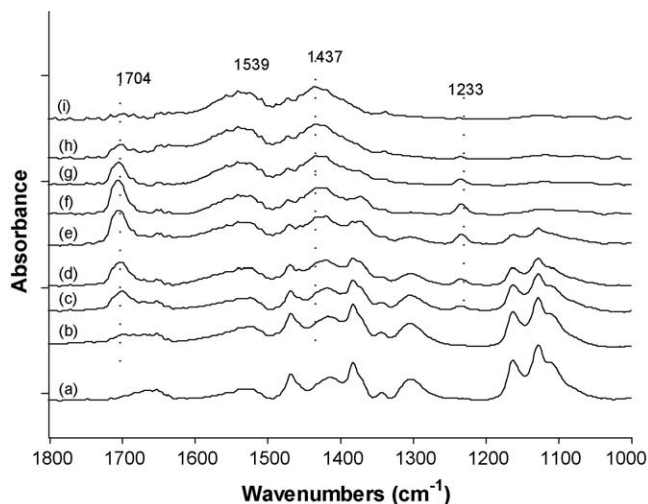
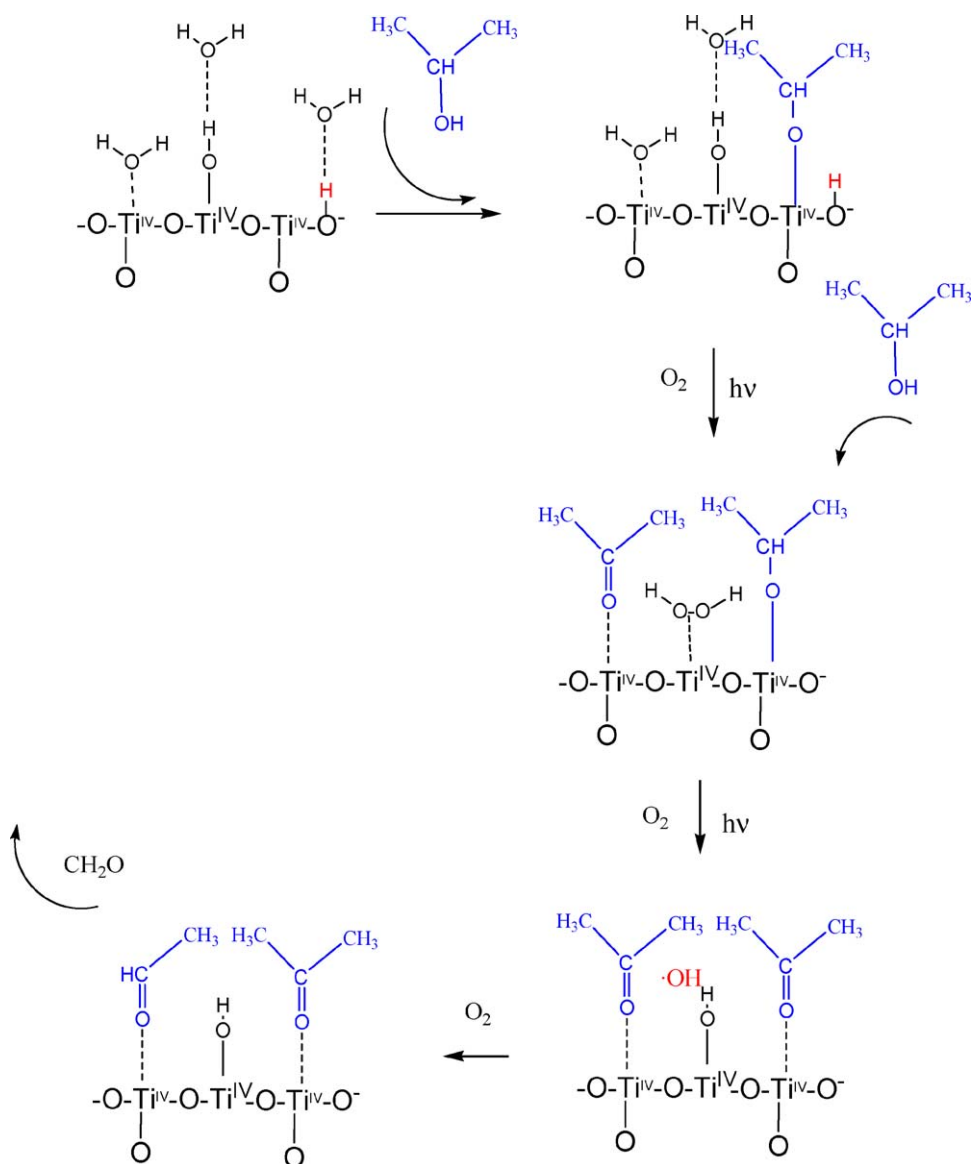


Fig. 8. FTIR spectra of 2-propanol adsorbed on Hombikat (a) and after 2 (b), 5 (c), 10 (d), 15 (e), 20 (f), 25 (g), 30 (h) and 35 (i) minutes of illumination.

centres can act with photogenerated electrons capture centres and delay the recombination rate of electron/hole pair [56]. It has also been indicated that these oxygen defects could be located in the vicinities of rutile–anatase border [56]. This could be the main cause of the rapid photocatalytic degradation provided by TiO₂-P25 respect to that observed in Hombikat which presents only the anatase phase.

In the spectra obtained with Hombikat and 2-propanol during the first 15 min of illumination (Fig. 8), the gradual formation of a band at 1233 cm^{−1} attributed to acetone and another one centred at 1704 cm^{−1} with a shoulder at 1709 cm^{−1}, attributed to νC=O vibration, can be observed. The presence of this dual band is attributed to acetone and other aldehydes such as acetaldehyde or formaldehyde generated during the process. In other words, differently from the observed with the TiO₂-P25 it seems that Hombikat is able to degrade 2-propanol and the generated acetone simultaneously. It should be noted that after the first 20 min of illumination only the bands of acetates (1539 and 1437 cm^{−1}) were clearly observed, just when no 2-propanol remained on the surface of the catalyst. The region of the hydroxyl groups (Fig. 9) shows a steady formation and disappearance of the bands centred at 3400 and 3200 cm^{−1}. These bands correlate with those of



Scheme 2.

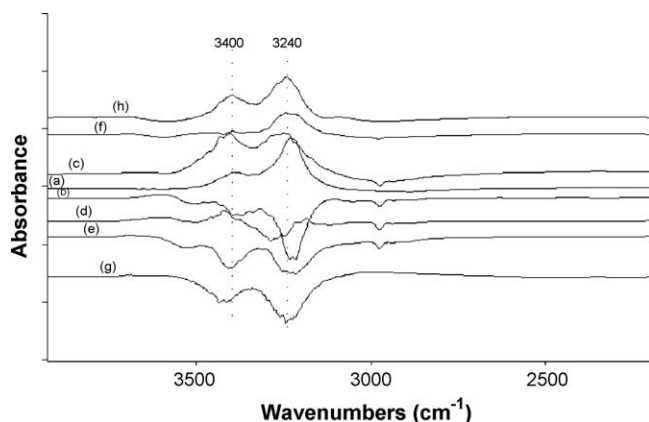
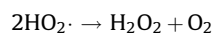
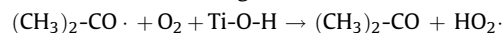


Fig. 9. Modification of relative intensity of FTIR spectra in the hydroxyl group region of Hombikat under illumination: (a) after the first 2 min and after every 5 min (b–g). These spectra have been obtained by subtracting that of the previous illumination period (shown in Fig. 8) from each spectrum.

adsorbed H_2O_2 [57,58]. Considering FTIR and degradation study results, the degradation mechanism of 2-propanol with Hombikat could be summarized in Scheme 2. Molecules of 2-propanol adsorb near to centres in which water molecules adsorb by means of hydrogen bonds with acid hydroxyl groups (Fig. 5). Interaction of the alcohol's molecules causes desorption of these water molecules. Illumination of the sample produces acetone which may be adsorbed at different centres leaving the above mentioned centres available for the adsorption of new molecules of 2-propanol. Irradiation also generates hydrogen peroxide (Fig. 9) by means of the following reaction:



In this catalyst, rutile phase is not present which allows the diffusion of photogenerated e^- and thus slow down the recombination rate of e^-/h^+ pair. This would explain the slower degradation of the alcohol in comparison to that with TiO_2 -P25. H_2O_2 molecules adsorbed on the surface of Hombikat under illumination can react with photogenerated electrons to give $\cdot\text{OH}$ radicals which degrade acetone while newly 2-propanol molecules are adsorbed. Therefore, a continuous degradation of 2-propanol and acetone was observed.

As observed in the FTIR studies, only when all the molecules of 2-propanol have reacted the formation of acetates occurs. These acetates can be responsible for the observed deactivation of the catalyst. As in the degradation studies there was always a 2-propanol atmosphere, no deactivation took place.

The particle size of this catalyst is smaller than that of TiO_2 -P25, which can also be responsible for the slower degradation provided by Hombikat as observed in FTIR study. However, in this catalyst FTIR studies have revealed, in addition to the degradation of 2-propanol, side reactions of formation of H_2O_2 that seems to improve the efficiency of the process. These side reactions can explain the activation process observed in this catalyst in experiments in continuous.

7.5. Behaviour of 2-propanol adsorbed on the Millennium under illumination

The spectra obtained from the behaviour of 2-propanol adsorbed on Millennium under illumination (Fig. 10) are similar to those of Hombikat during the first 20 min. However, after this

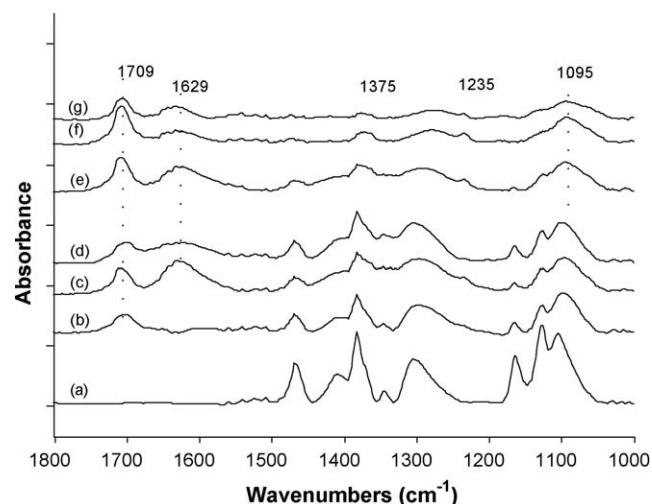


Fig. 10. FTIR spectra of 2-propanol adsorbed on Millennium (a) and after 2 (b), 5 (c), 10 (d), 15 (e), 20 (f) and 30 (g) minutes of illumination.

irradiation time new bands (between 1709 – 1095 cm^{-1}) which correlate with those of acetaldehyde, were observed. These bands became gradually decreased and the formation of acetates was not observed. This means that in this case a similar mechanism to that of Hombikat can be proposed.

7.6. Behaviour of 2-propanol adsorbed on s/g- TiO_2 under illumination

Fig. 11 shows the spectra obtained with s/g- TiO_2 under illumination. During the first 2–10 min of irradiation, new bands at 1649 and 1270 cm^{-1} not observed in previous studies, were obtained. After 30 min other new bands at 1709 and 1235 cm^{-1} that correlate with those of acetone were generated. The band present at 1649 cm^{-1} is typical of olefinic compounds and the final spectrum obtained after 30 min is very similar to that of acrolein. In this catalyst, as in TiO_2 -P25 and Hombikat, characterization studies by ammonia adsorption identified the presence of Lewis acid centres. The presence of these centres was attributed to the formation of propylene by interaction of 2-propanol with TiO_2 -P25 and Hombikat. Propylene was not observed in the interaction of the alcohol with s/g- TiO_2 . However, it seems that irradiation leads

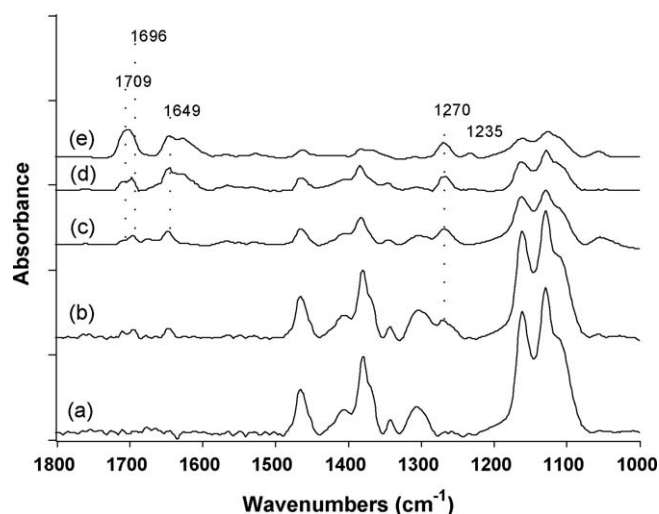
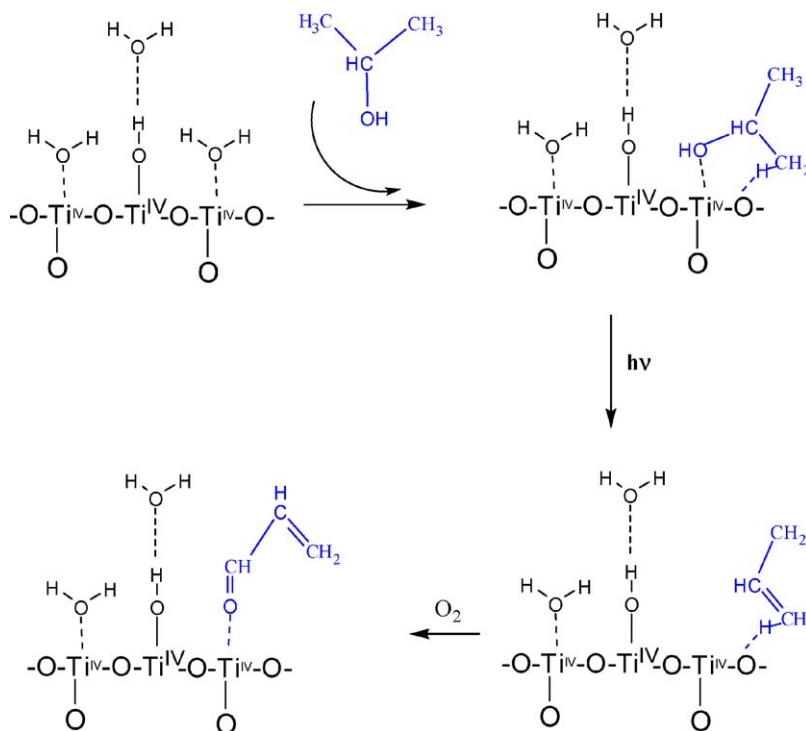


Fig. 11. FTIR spectra of 2-propanol adsorbed on s/g- TiO_2 (a) and after 2 (b), 10 (c), 20 (d) and 30 (e) minutes of illumination.



Scheme 3.

to the simultaneous dehydration and photocatalytic degradation of the molecule. Thus, Scheme 3 is proposed for the degradation of 2-propanol in gas phase.

A fast deactivation of this catalyst was observed in the system in continuous. This can be justified by the fact that acrolein can evolve into acrylic acid that might be responsible for deactivation.

8. Conclusions

The present work has revealed that different distributions of surface hydroxyl groups and Lewis or Brönsted acid centres alter the photocatalytic degradation, i.e., mechanism and efficiency, of 2-propanol in gas phase.

FTIR studies have shown that the alcohol molecule was more readily degraded by TiO_2 -P25 than by the other catalysts tested. However, this catalyst underwent deactivation processes, probably due to acetate adsorption which led to the slowing down of the overall degradation.

FTIR analyses have also indicated that during the photocatalytic degradation of 2-propanol H_2O_2 can be generated. This would result in a different degradation mechanism. This oxidizer has been observed especially in Hombikat and Millennium, which provided slower degradation of 2-propanol as FTIR measurements indicated. However, in the experiments in continuous the efficiency obtained with Hombikat was higher than that of TiO_2 -P25. In the latter no deactivation was observed, probably due to the progressive involvement of H_2O_2 in the mechanism.

The catalyst $s/g\text{-TiO}_2$ was poorly active but stable, probably due to the different degradation mechanism exhibited.

The catalyst Kemira presented a similar hydroxyl group distribution to that of TiO_2 -P25 and $s/g\text{-TiO}_2$. However, no Lewis acid centres were detected in Kemira, which may be caused by the absence of anatase phase. The nil adsorption and degradation of 2-propanol observed with this catalyst could also be related to the absence of such centres.

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